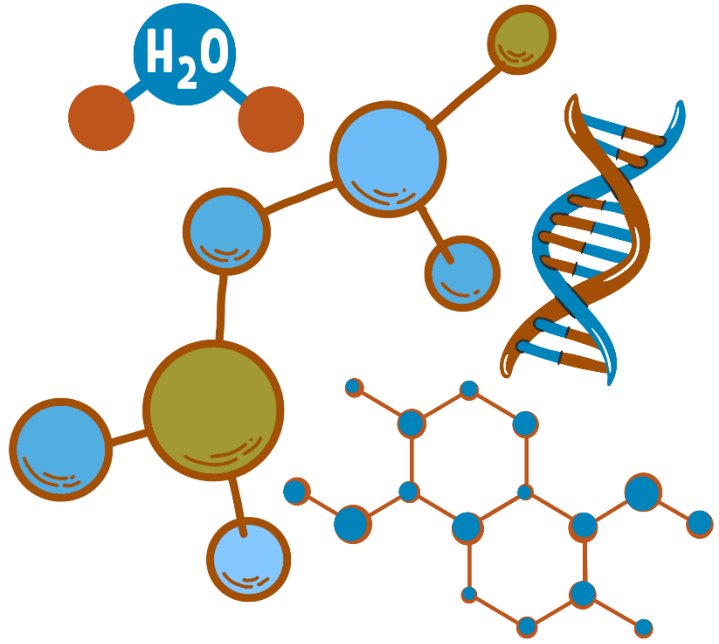
Principles of Organic Chemistry I
CHEM 244

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Chapter 4: Physical Properties and Intermolecular Forces



Chapter 4: Physical Properties and Intermolecular Forces

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1. Physical Property

A physical property is defined as a characteristic of a substance that can be observed or measured without changing its chemical identity.

Examples; physical properties include color, density, the states of matter (gas, liquid, solid) , melting point, and boiling point.

2. Types of Intermolecular Forces

2.1. Intermolecular forces (van der Waals forces)

- **Van der Waals forces are a type of intermolecular force that includes weak attractions between molecules.**
- **Van der Waals force occur between all atoms and molecules, including nonpolar ones.**
- **The forces that act between molecules are not as strong as those between ions.**
- **The relative surface area of the molecules;**
  - **Branching decrease such forces and therefore, decreasing boiling point.**
  - ***Example;***

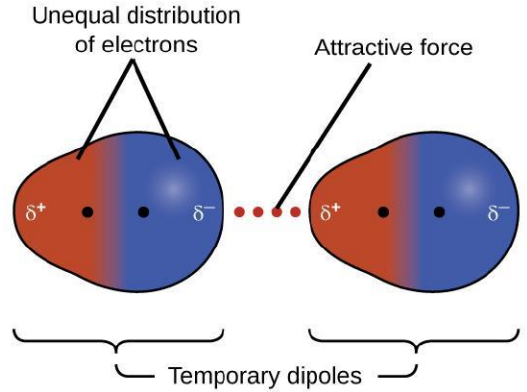
    Pentane ($CH_3CH_2CH_2CH_2CH_3$) has a boiling point of 36.1 °C and Neopentane ($C(CH_3)_4$) has a boiling point of 9.5 °C.

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2. Types of Intermolecular Forces

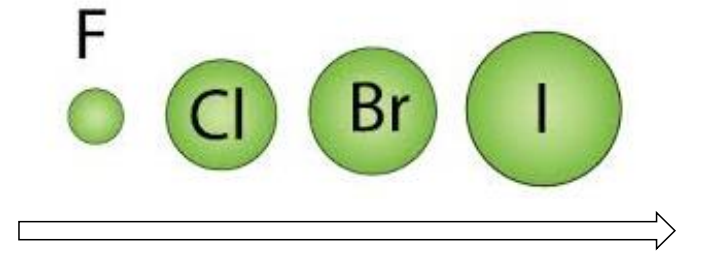
2.2. London Dispersion Forces

- **London or Dispersion Forces result when a temporary dipole in a molecule caused by a momentary shifting of electrons induces an opposite and also temporary dipole in an adjacent molecule causing a weak attraction between the two molecules.**
- **Molecules which rely only on dispersion forces generally have low melting points and boiling points.**



- **The relative polarizability of electrons of the atoms;**
  - **The electrons of large atoms such as iodine are loosely held and are easily polarized, whereases the electrons of small atoms such as fluorine are more tightly held and are much less polarizable.**
  - ***Example;***

    HI has a boiling point of -35 °C whereas HF has a boiling point of 19.5 °C.



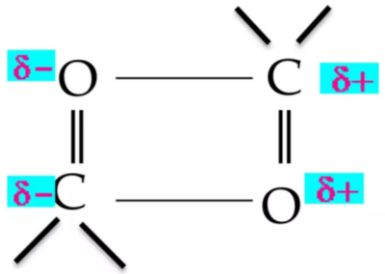
Polarizability increases with increasing size

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2. Types of Intermolecular Forces

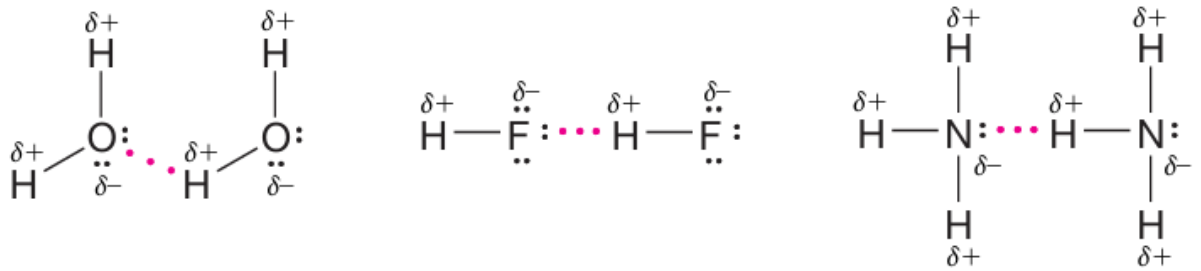
2.3. Dipole-dipole Forces

- Dipole-dipole forces refers to the electrostatic forces between two permanent polar molecules.
- There is an interaction between δ+ and δ- areas in each molecule; these are much weaker than ion-ion forces.



2.4. Hydrogen Bonds

- Hydrogen bond is very strong dipole–dipole attractions occur between hydrogen atoms bonded to small, strongly electronegative atoms (N, O, or F) and nonbonding electron pairs on other electronegative atoms.



The red dots represent a hydrogen bond.

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2. Types of Intermolecular Forces

2.4. Hydrogen Bonds

- **Hydrogen bonds consist of two types:**

  1) Intermolecular hydrogen bonds:

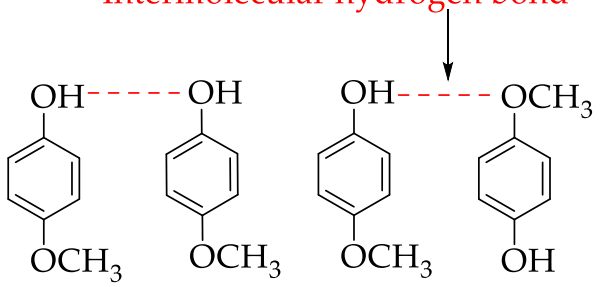
  Occur between separate molecules in a substance.

  2) Intramolecular hydrogen bonds:

  Occur within one single molecule.

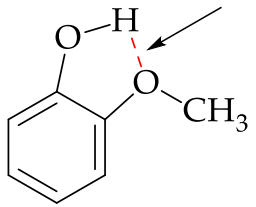
- **Generally, Intramolecular hydrogen bonding reduces intermolecular interactions, which generally lowers melting point, boiling point, and solubility compared to compounds capable of intermolecular hydrogen bonding.**

Intermolecular hydrogen bond



***p*-Methoxyphenol**
m.p = 243 °C

Intramolecular hydrogen bond



***o*-Methoxyphenol**
m.p = 204-206 °C

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3. Physical Properties of Hydrocarbons

- **Hydrocarbons are nonpolar compounds and thus, the dispersion forces controlling their physical properties.**
- **Physical state;**

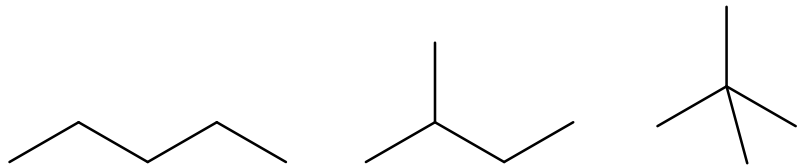
  C1–C4 Hydrocarbons are gases, C5-C17 hydrocarbons are liquids, and hydrocarbons with C18 or higher are wax-like solids.

- **Boiling points and Melting points:**

  Effect of Molecular weight; **Increasing the molecular weight will increase, the boiling point and melting point increase.**

  - ***Example;*** **Methane (CH_4) has a boiling point of -162 °C whereas ethane (CH_3CH_3) has a boiling point of -88.2 °C.**

  Effect of Branching; **Increasing the degree of branching in an alkane decreases its boiling point.**



Pentane
b.p 36 °C
m.p -130 °C

Isopentane
b.p 28 °C
m.p -160 °C

Neopentane
b.p 10 °C
m.p -17 °C

- **Solubility:**

  Hydrocarbons as nonpolar compounds are soluble in nonpolar solvents such as carbon tetrachloride and benzene, but insoluble in polar solvents like water.

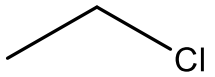
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3. Physical Properties of Alkyl Halides (Haloalkanes)

- **Boiling points;**
  - **Boiling points generally increase with molecular mass and halogen size:**

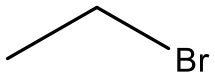
$$R–F < R–Cl < R–Br < R–I$$

  - **Branching decreases boiling points.**



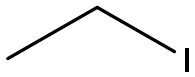
Chloroethane

bp 12.3 °C
(MW = 64.51)



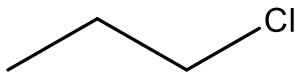
Bromoethane

bp 38.4 °C
(MW = 108.97)



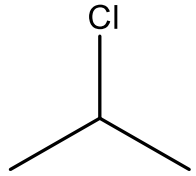
Iodoethane

bp 72.3 °C
(MW = 155.97)



1-Chloropropane

bp 46.6 °C
(MW = 78.54)



2-Chloropropane

bp 35.7 °C
(MW = 78.54)

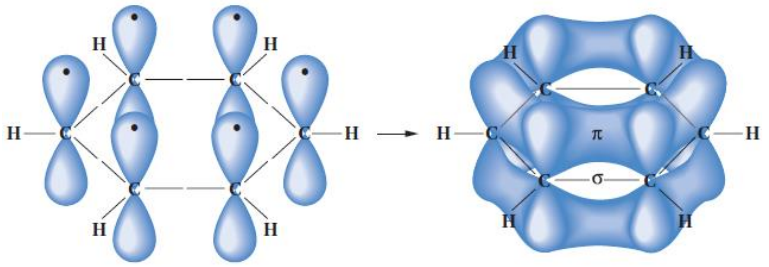
- **Solubility;**
  - **Alkyl halides are poorly soluble in water but soluble in organic solvents.**
  - **Water solubility generally decreases as the hydrocarbon portion increases**

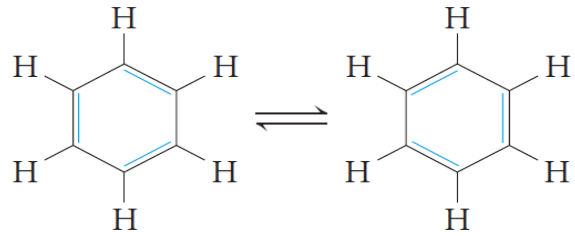
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4. Resonance and Delocalization

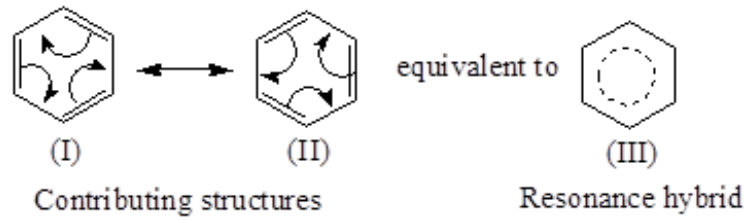
4.1. The Resonance Explanation for the Structure of Benzene

- **Resonance** is defined as a way of describing bonding in certain molecules or ions by the combination of several **contributing structures or forms** (commonly call **resonance structures**).
- **Benzene** is an aromatic molecule that has the molecular formula of (C_6H_6) which a ratio of (1:1) between carbon and hydrogen atoms indicating a highly unsaturated structure.
- **Kekulé** proposed that Benzene has **six-carbon atoms** that are located in the center of a regular **hexagon one hydrogen** atom attached to each carbon atom.
- His suggestion shows an **alternation between single and double bonds** through the ring via a conjugated system of double bonds.





The Kekulé structures for Benzene



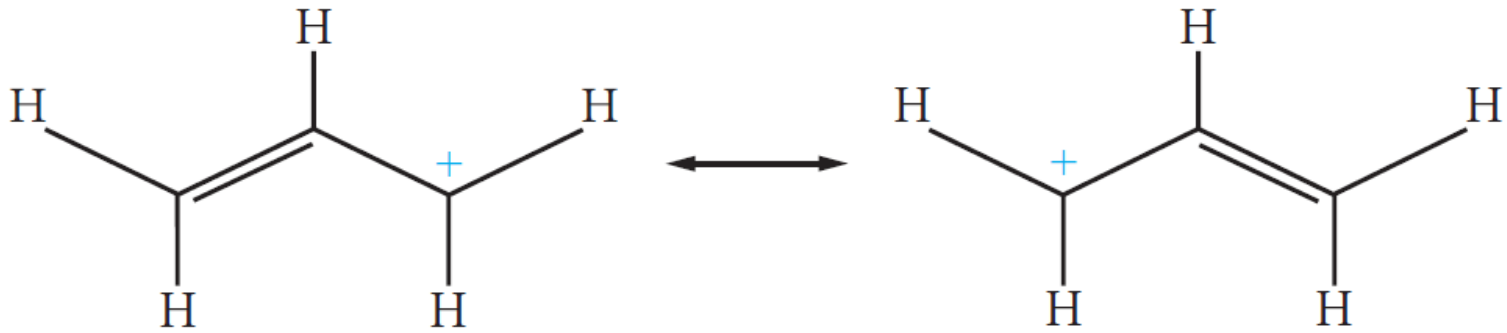
Resonance Model for Benzene

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4. Resonance and Delocalization

4.2. Resonance Stabilization of Allylic Carbocations

- **An allylic carbocation is a carbocation in which the positively charged carbon is adjacent to a carbon–carbon double bond.**
- **The positive charge is delocalized over the two terminal carbon atoms of the allylic system through resonance.**
- **This delocalization stabilizes the allylic carbocation.**



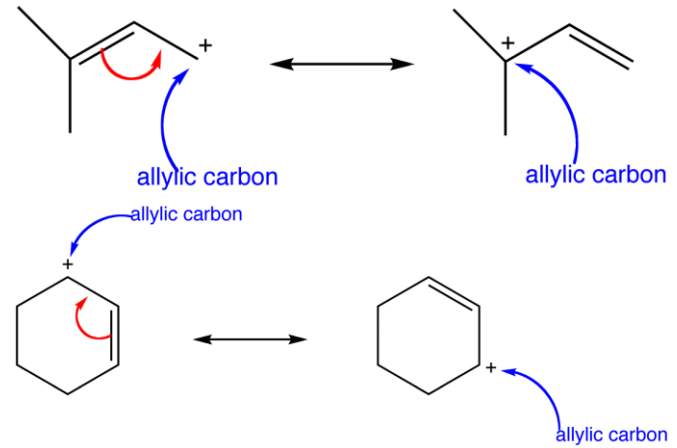
the allyl carbocation

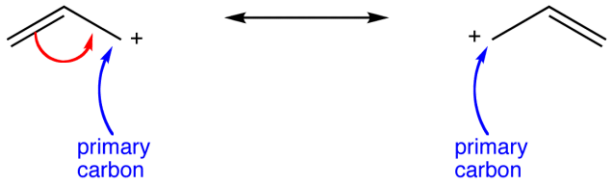
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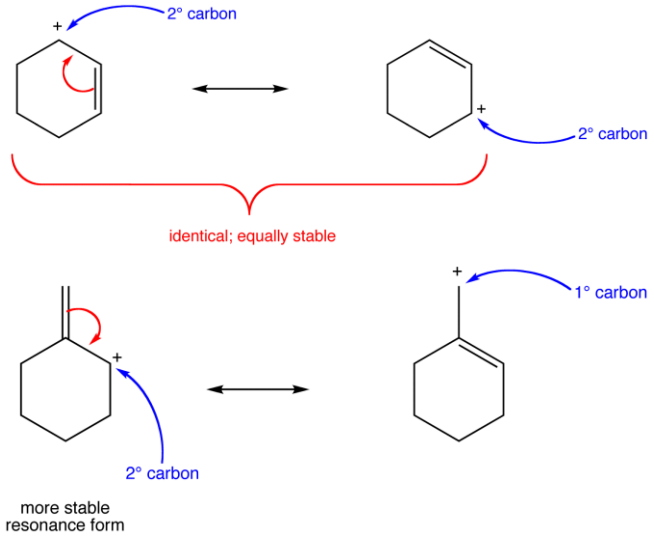
4. Resonance and Delocalization

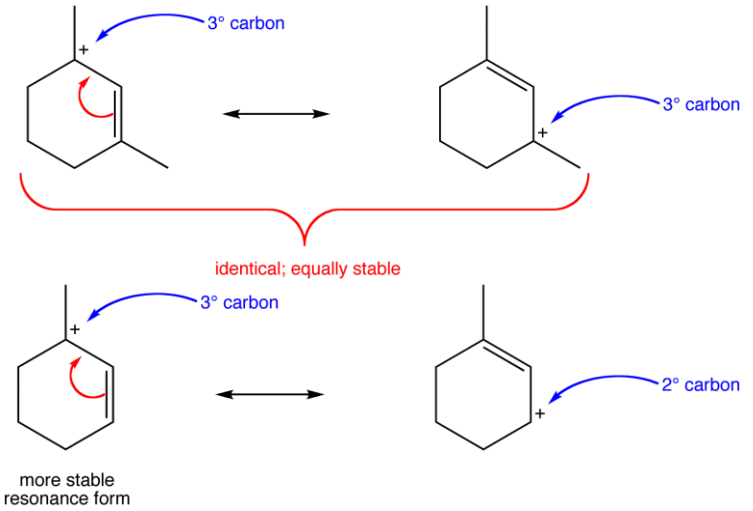
4.3. Resonance and Classification of Allylic Carbocations

- **Allylic carbocations can be represented by two resonance contributors that differ in the position of the double bond and the positive charge.**
- **The positively charged carbon in a resonance contributor may be primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbon atoms directly attached to it.**
- **The degree of substitution at the positively charged carbon may differ between resonance contributors.**







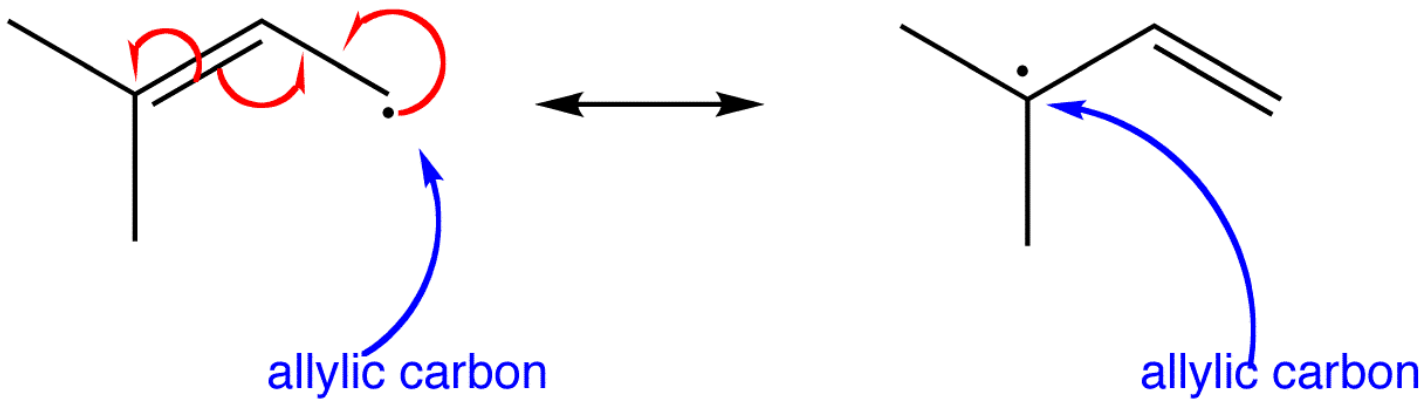


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4. Resonance and Delocalization

4.4. Resonance Stabilization of Allylic Radicals

- An allylic radical is a radical in which the carbon bearing the unpaired electron is adjacent to a carbon–carbon double bond.
- The unpaired electron is delocalized over the two terminal carbon atoms of the allylic system through resonance.
- This delocalization contributes to the stability of the allylic radical.

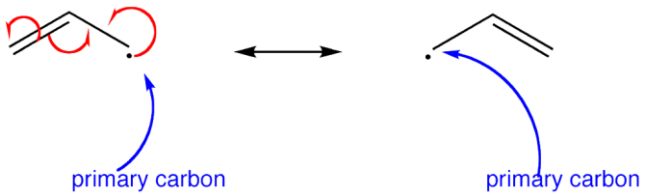


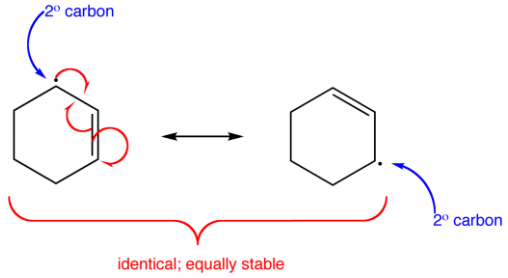
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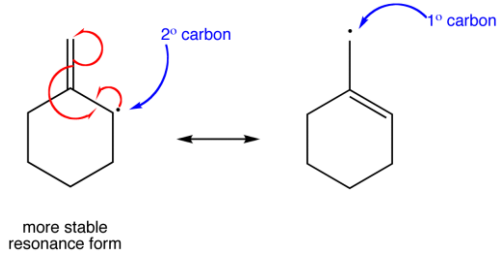
4. Resonance and Delocalization

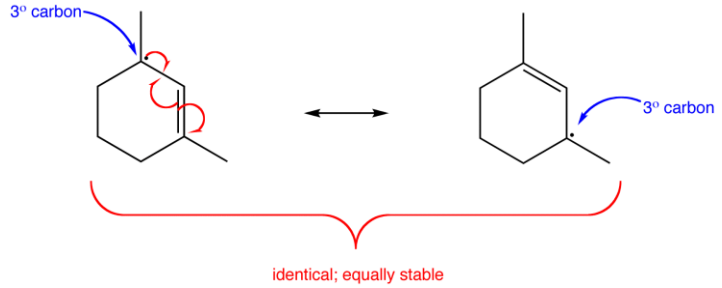
4.5. Resonance and Classification of Allylic Radicals

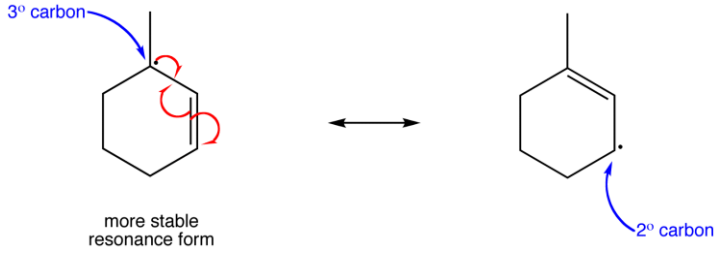
- **Allylic radicals can be represented by two resonance contributors that differ in the position of the double bond and the unpaired electron.**
- **The radical-bearing carbon in a resonance contributor may be primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbon atoms directly attached to it.**
- **The degree of substitution at the radical-bearing carbon may differ between resonance contributors.**









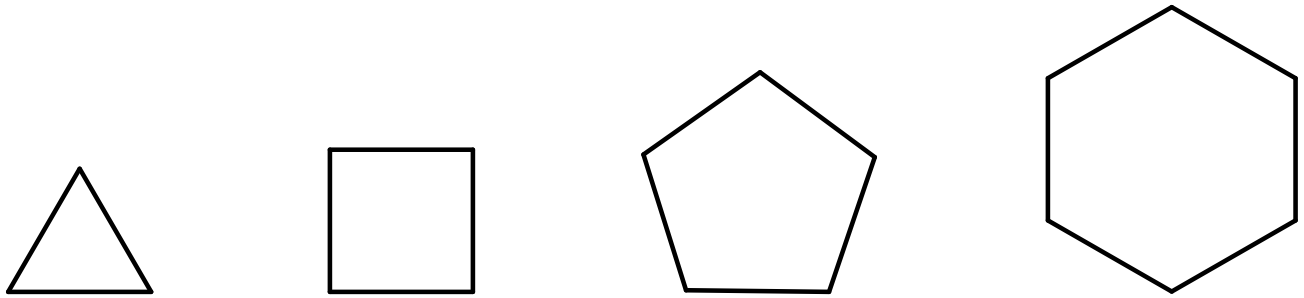


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5. Ring Strain and Stability of Cycloalkanes

5.1. Ring Strain in Cycloalkanes

- **Ring Strain is a type of instability that exists when bonds in a molecule form angles that are abnormal.**
- **Baeyer suggested that the stability of a cycloalkane could be predicted by determining how close the bond angle of a planar cycloalkane is to the ideal tetrahedral bond angle of 109.5°.**
- **Strain is most commonly discussed for small rings, such as cyclopropanes and cyclobutanes.**



60° **90°** **108°** **109.5°**

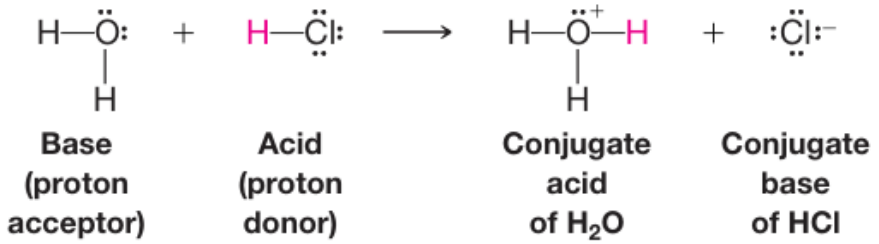
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6. Acids and Bases

6.1. Bronsted–Lowry Acids and Base

Brønsted–Lowry acid–base reactions involve the transfer of protons.

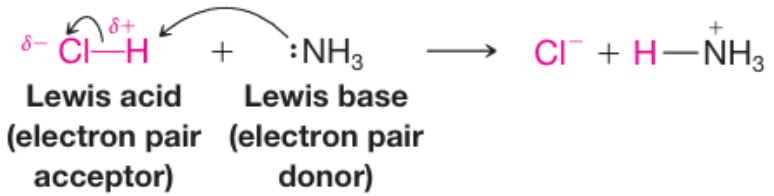
- **Brønsted–Lowry acid is a substance that can donate (or lose) a proton.**
- **Brønsted–Lowry base is a substance that can accept (or remove) a proton.**

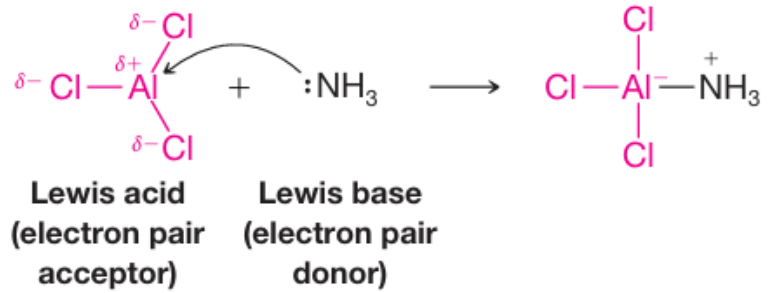


6.2. Lewis Acids and Bases

In Lewis acid–base theory, proton donors are not the only acids.

- **Lewis's acid is electron pair acceptors (i.e., any electron-deficient atom and that have atoms with vacant orbital).**
- **Lewis's base is electron pair donors (i.e. Any electron-rich atom).**





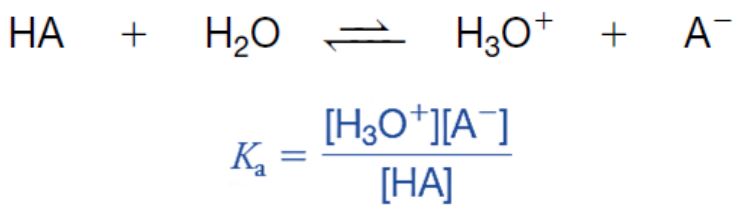
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6. Acids and Bases

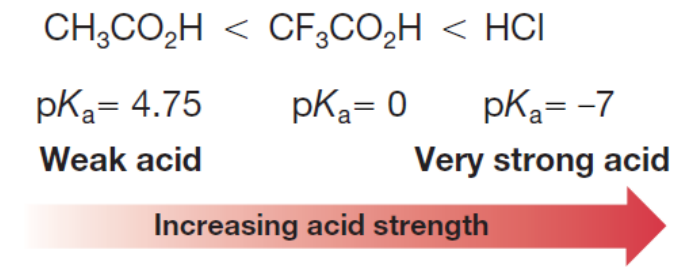
6.3. The Strength of Brønsted–Lowry Acids and Bases: Ka and pKa

A) The Acidity Constant, K_a

- For any weak acid dissolved in water. Using a generalized hypothetical acid (HA), the expression for the acidity constant is:



- Generally;
  - A large value of K_a means the acid is a strong acid.
  - A small value of K_a means the acid is a weak acid.

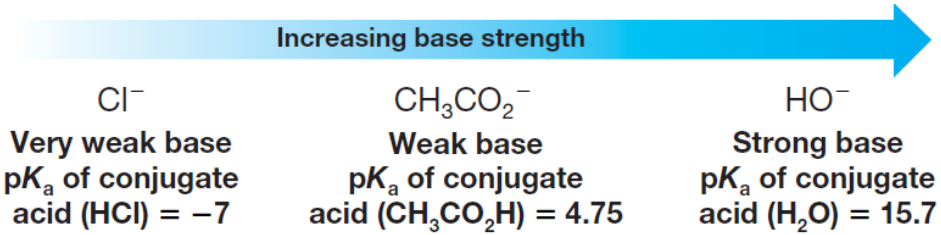


B) Acidity and pK_a

- The acidity constant, K_a, expressed as its negative logarithm, pK_a:

$$pK_a = -\log K_a$$

- The larger the value of the pK_a, the weaker is the acid.
- The stronger the acid, the weaker will be its conjugate base.



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6. Acids and Bases

6.4. Relationships Between Structure and Acidity

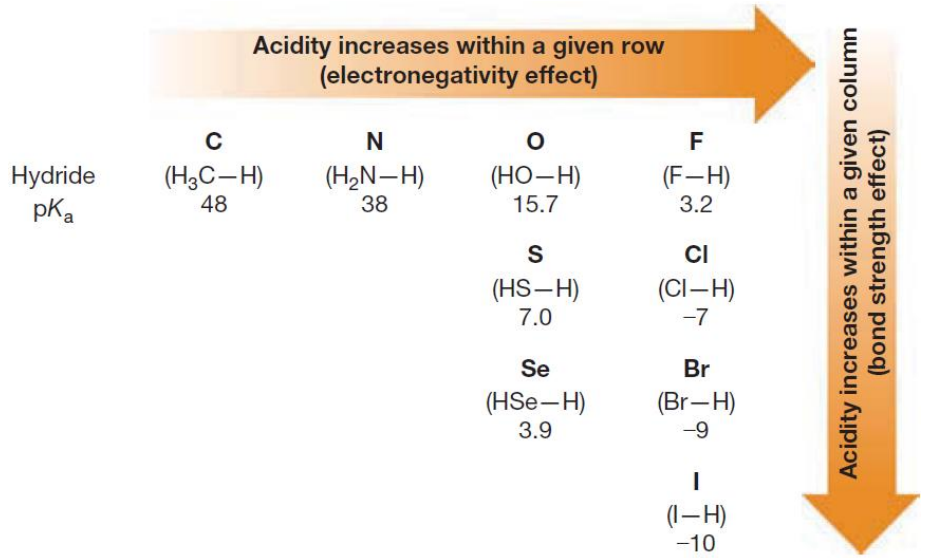
A) Periodic Table Trend

- **Bond Strength To The Proton**

  Acidity increases from top to bottom in each column with decreasing bond strength.

- **Electronegativity of The Atom Bonded To The Hydrogen**

  Acidity increases from left to right across a given row with increasing electronegativity.



B) The Effect of Hybridization

- **A *sp* carbon atom is effectively more electronegative than a sp^2 carbon, which in turn is more electronegative than a sp^3 carbon.**
- **Example; Alkyne hydrogen is weakly acid and Alkene, and alkane hydrogens are essentially not acidic.**

Relative Acidity of the Hydrocarbons

$$HC{\equiv}CH > H_2C{=}CH_2 > H_3C{-}CH_3$$

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6. Acids and Bases

6.4. Relationships Between Structure and Acidity

C) Inductive Effects

- The electron withdrawing increases acidity. Electron-withdrawing substituents (-I); -OH, -SH, -CHO, -$COCH_3$, -COOH, -NO_2, -NH_2, -OCH_3
- The electron donating decreases acidity, Electron-donating substituents (+I); -CH_3, -C_2H_5

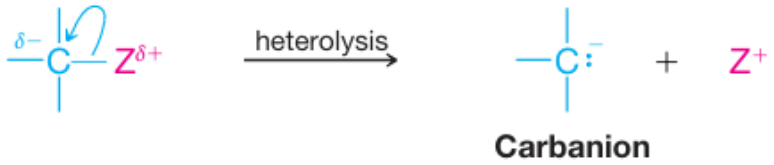
6.5. Heterolysis of Bonds to Carbon: Carbocations and Carbanions

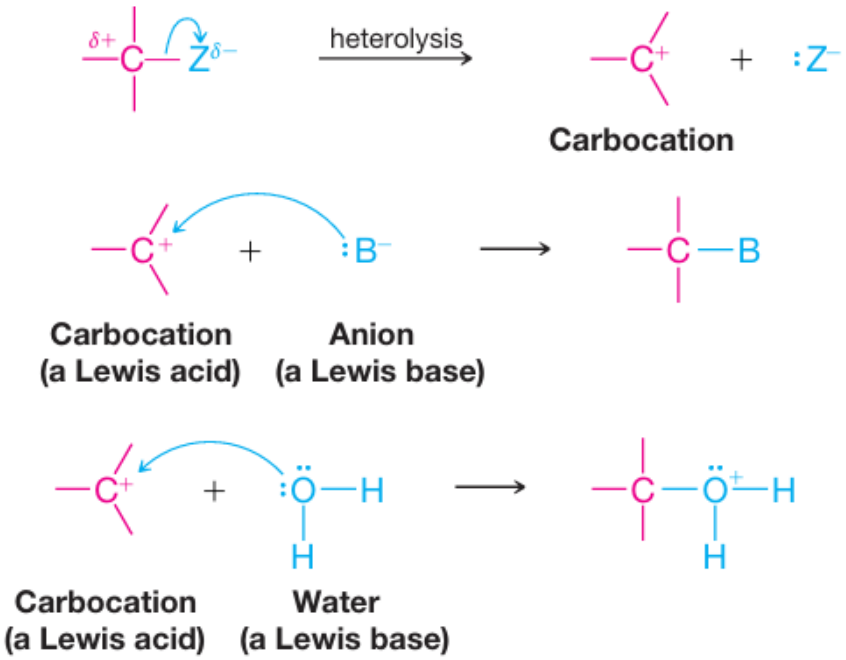
Heterolysis of a bond to a carbon atom can lead to either of two ions:

- A carbocation; an ion with a positive charge on the carbon atom.

  Example; Carbocations are electron deficient, and therefore carbocations are Lewis's acids.
- A carbanion; an ion with a negatively charged on the carbon atom.

  Example; Carbanions are electron rich (have an unshared electron pair) and therefore, carbanions are Lewis bases.





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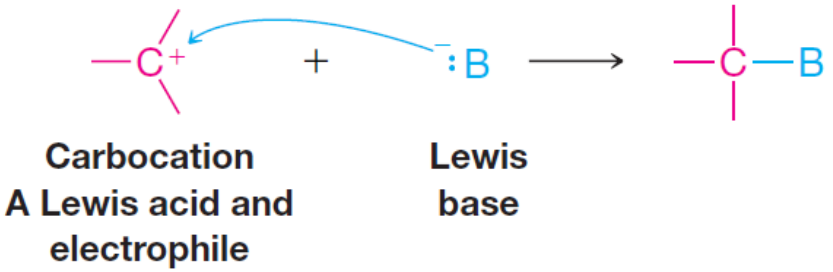
6. Acids and Bases

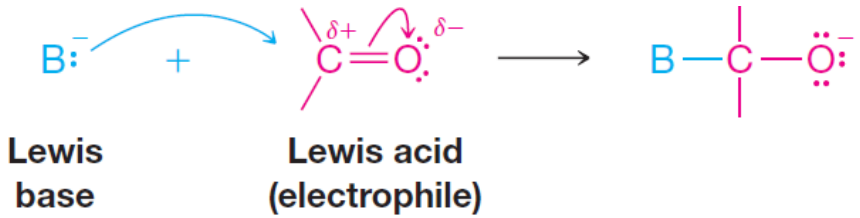
6.6. Electrophiles and Nucleophiles

- **Electrophiles** are reagents that seek electrons.

Examples;

- Lewis's acids (electron pair acceptors).
- Carbocations.
- Carbon atoms that are electron poor because of bond polarity (i.e. Carbonyl carbon).

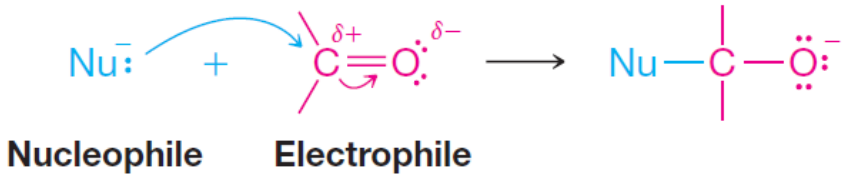


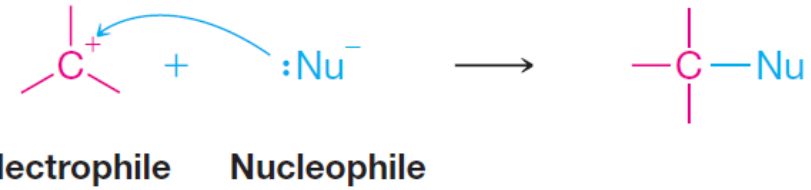


- **Nucleophile** is a Lewis base that seeks a positive center such as a positively charged carbon atom.

Examples;

- Lewis bases (electron pair donors).
- Carbanions.





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6. Sources of Alkanes

- The two principal sources of alkanes are petroleum and natural gas.

6.1. Petroleum

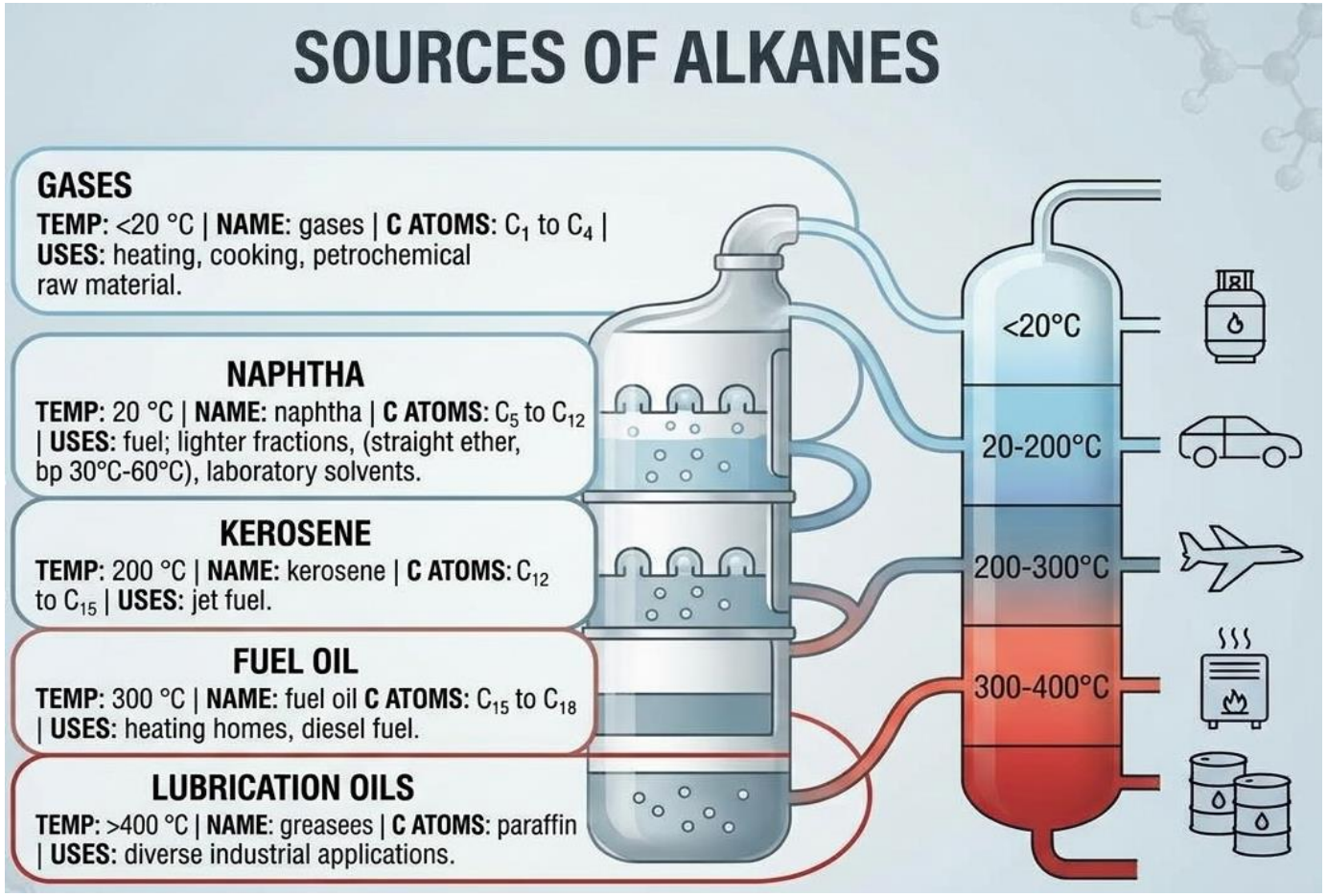
- Petroleum is at present our most important fossil fuel.
- Petroleum is a complex mixture of hydrocarbons formed over eons of time through the gradual decay of buried animal and vegetable matter.
- Crude oil is a viscous black liquid that collects in vast underground pockets in sedimentary rock.
- It must be brought to the surface via drilling and pumping. To be most useful, the crude oil must be refined.
- The first step in petroleum refining is usually distillation.

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6. Sources of Alkanes

6.1.1 Petroleum Refining

- **Petroleum refining** is the process of separating crude oil into fractions based on their boiling points, followed by further treatment to remove impurities and improve product quality.
- During fractional distillation, the most volatile components are collected at lower temperatures, while less volatile components are collected at higher temperatures. The heaviest fractions remain as residues.
- **Refined petroleum** products are used as fuels, lubricants, and raw materials for the petrochemical industry, which produces plastics, synthetic fibers, and other useful chemicals.



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6. Sources of Alkanes

6.1.2 Octane Number and Fuel Performance

- The octane number (octane rating) measures a gasoline fuel's resistance to engine knocking (premature autoignition).
- Isooctane (2,2,4-trimethylpentane) is assigned an octane number of 100, while n-heptane is assigned a value of 0.
- The octane number is determined by comparing the knocking characteristics of gasoline with those of reference mixtures of isooctane and n-heptane.
- Example: Gasoline with an octane number of 90 has knocking characteristics equivalent to a mixture of 90% isooctane and 10% n-heptane by volume under standard test conditions.
- Branched-chain alkanes generally have higher octane numbers than straight-chain alkanes. For straight-chain alkanes, octane numbers generally decrease as chain length increases.
- The octane number can be improved by blending gasoline with high-octane components or suitable antiknock additives.
- Tetraethyllead, $Pb(C_2H_5)_4$, was historically used as an effective antiknock additive but was phased out of road gasoline because of its toxic and environmental effects.

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6. Sources of Alkanes

6.2 Natural Gas

- Natural gas is a mixture of low-molecular-weight alkanes, mainly C_1–C_4 hydrocarbons.
- It consists primarily of methane (80–95%), along with ethane, propane, butane, higher hydrocarbons, and small amounts of non-hydrocarbon gases such as nitrogen.
- Natural gas is generally a cleaner-burning fuel than petroleum-derived liquid fuels.
- Propane and butane can be separated from natural gas, liquefied under pressure, and stored in cylinders as liquefied petroleum gas (LPG).
- Propane is a major component of LPG. Liquefaction significantly reduces its volume, making storage and transportation easier.
- Natural gas is also an important raw material for producing organic chemicals, including alcohols, aldehydes, ketones, carboxylic acids, and alkyl halides.

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7. Practice Problems

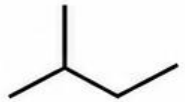
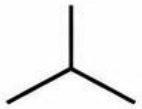
1. Physical state (alkanes)

Which of the following alkanes is most likely to be a liquid at room temperature (25 °C)?

A) CH_4
B) $CH_3CH_2CH_3$
C) $CH_3(CH_2)_5CH_3$
D) $CH_3(CH_2)_{12}CH_3$

2. Branching and boiling point (alkanes)

Which isomer of C_5H_{12} is expected to have the lowest boiling point?

A) 
B) 
C) 
D) 

3. Boiling point and halogen size

Which alkyl halide is expected to have the highest boiling point?

A) CH_3F
B) CH_3Cl
C) CH_3Br
D) CH_3I

4. Intermolecular forces (alkanes)

Which compound is expected to have the highest boiling point?

A) CH_3CH_3
B) $CH_3CH_2CH_3$
C) $CH_3CH_2CH_2CH_3$
D) $CH_3CH(CH_3)CH_2CH_3$

5. Acidity and hybridization

Which of the following compounds has the most acidic hydrogen (lowest pK_a)?

A) CH_3CH_3
B) $CH_2{=}CH_2$
C) $CH_3C{\equiv}CH$
D) $CH_3CH_2CH_3$

6. Electron-withdrawing and -donating groups

Which of the following substituents is an electron-withdrawing group (−I effect)?

A) $-CH_3$
B) $-C_2H_5$
C) $-NO_2$
D) $-OCH_3$